

Special Methods for Overcoming Data Collection Problems in XAFS

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Methods of Preparing Transmission Samples

One must avoid effects of excess thickness or sample non uniformity. See “Thickness effect on the extended – x – ray- absorption- fine- structure amplitude”; E.A. Stern and K. Kim, PRB 23, 1981, 3781. The “edge of interest” step height should be no more than

$$(1) \quad \Delta\mu x \sim 1.5$$

1. Brittle Samples

Usually one can grind extensively in an agate mortar and pestle, almost to a paste, until by microscopic examination one reaches a condition such that there is a mixture consisting of an occasional maximum particle diameter as much as ~ 20 microns mixed in with mostly much smaller particles. The mixture can be painted onto scotch tape or Kapton tape with a q tip or solder brush, and several layers combined to satisfy (1) above.

One can often by these means satisfy the thickness requirements as tested by experimental measurement, and the XAFS is found to be consistent for different thicknesses and positions of samples. More uniform samples may be necessary and can be obtained by sieving or fractionation. See the Grant Bunker web site

http://gbxafs.iit.edu/training/xafs_sample_prep.pdf

(Of course, detuning the beam to remove harmonics can lessen thickness effect problems.)

2. Ductile Alloys

One can roll many times in a rolling mill, interspersed with stress anneals in evacuated quartz tubes between rolling sessions. One can check for the appearance of pinholes with a bright light in a dark room, and test for thickness uniformity with the appropriate thin film thickness feeler gauge. Once film is about 30 microns thick, an alternative method is final electropolishing, in many cases.

Electropolishing recipes are discussed, for example in :

“The Electrolytic and Chemical Polishing of Metals in Research and Industry” by W.J. Tegart, Pergamon Press (1959)

3. Anisotropic Samples

For non - cubic materials the XAFS signal may depend on the relative orientation of the electric vector with the c axis. If one has a powder formed by grinding, the orientation of the crystalline cells packed onto a surface or tape may not be random. But a random powder is desirable so that one is sure of the interpretation. Anisotropic samples do not necessarily pack in a random way as determined by powder XRD. These problems are discussed in :

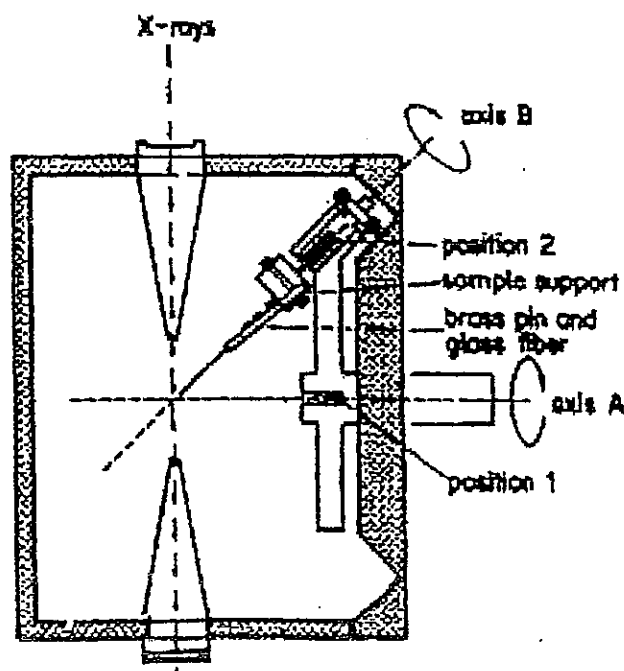
“X-Ray Diffraction Procedures” by H. Klug and L. Alexander, second edition, John Wiley, 1974

Preferred orientation can be reduced by prolonged grinding of the powders. *Reproducibility* of the orientation is enhanced by spinning. Dilution with small quantities of filler material such as flour helps reduce preferred orientation. Klug and Alexander also discuss various methods of mounting powders to minimize preferred orientation. One could test for preferred orientation effects in an EXAFS experiment by taking data varying the angle of the specimen relative to the incident beam.

There is another method that has been used successfully in sample characterization XRD that can produce random, smooth deBye Sherrer rings EVEN FOR A SINGLE CRYSTAL.. This is the Gandolfi technique.

See illustration below, and refer to A. Gruttner and K. Yvon, J. Appl. Cryst (1978) 11, 716. The sample is rotated about two axes at 45 degrees with each other, rotating at different angular speeds.

For XAFS, the speed of spinning about the two axes would need to be increased relative to that used in a powder camera. As far as I know no one has yet applied the Gandolfi method to XAFS but it might be a good idea, for certain applications.



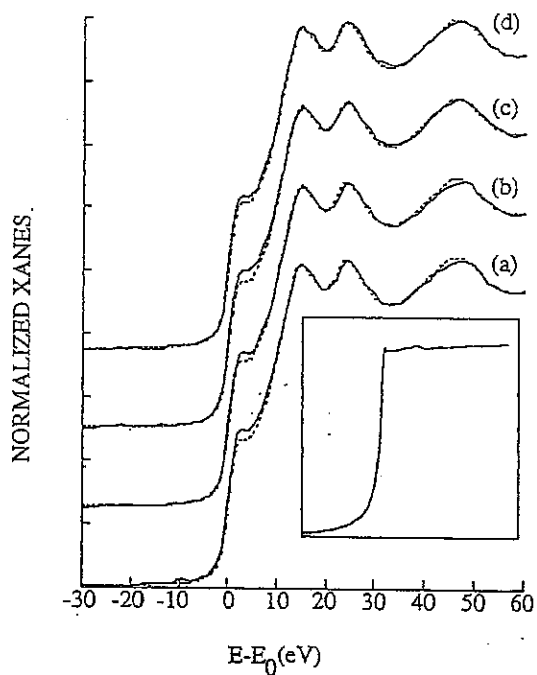
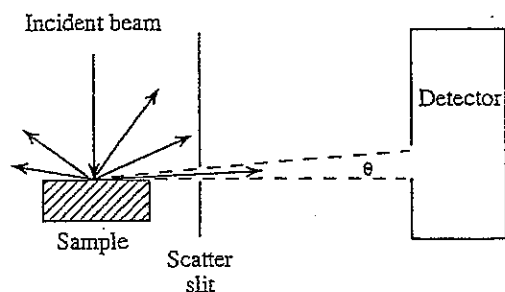
Distortions in Fluorescence XAFS: A Case Study

The usual motivation for obtaining XAFS in fluorescence is to detect dilute species. However, one may at times be motivated to use the technique on thick specimens. This produces a distortion in the XAFS signal. For my own self interest I much prefer a qualitative (no equations) explanation of this distortion.

Say one is at a photon energy corresponding to the “top” of an XAFS wiggle. Then the absorption coefficient is greater than for a photon corresponding to the “valley” of a wiggle. But in an infinite, concentrated specimen, both photons are absorbed with probability unity! So the question, at this simple level of explanation, is not why there is distortion, but why there is fine structure observed at all. The answer is that the photon at the “valley” of the wiggle goes further into the sample than the “top” of the wiggle photon and therefore the emitted fluorescence is attenuated less for the “valley” photon. But this is a relatively weak effect. So there will be a damping of the XAFS wiggles and a distortion in the fluorescence XAFS.

We were studying temperature dependent XAFS of metallic alloys based on FeAl, NiAl, and Co Al. These are neither brittle enough to grind into a fine powder (I don't think we tried grinding under liquid nitrogen) nor ductile enough to roll and we were unable to make transmission samples. We had no way of doing ϵ yield in our Displex temperature controller. The samples were concentrated so if fluorescence were to be used there would be a distortion. What to do?? The thought occurred...with a flat, polished specimen using normal incidence of the exciting beam, then if one restricted the out going rays to a *glancing emergent angle* one would be making the experiment look more like an ϵ yield experiment. This method was tried and found to work in that by using a simple

aluminum plate for a blocking shield plus scatter slit, one systematically removed more and more of the distortion as the emergent angle decreased. See the illustration of Cu XANES below, from Pease, et. al. :



Normalized XANES versus energy. Dashed curves are transmission data for comparison; (a) 2° detector with no scatter slit; (b) 2° detector with scatter slit; (c) 1° detector with no scatter slit; (d) 1° detector with scatter slit. Insert shows data over the same energy range using 45° incident, -45° exit geometry.

This is an easy technique to use to test for fluorescence distortions in specimens. Is a sample of species X in matrix Y sufficiently dilute in X? If the results are independent of emergent angle, it's probably o.k. There are now several excellent publications giving mathematical methods of correcting for the fluorescence distortion: A list of some of the literature is given below:

- (1) Pease, et. al. , Phys. Lett. A, 138, (1989), 230; Y. Suzuki, PRB 39, (1989), 3393 (experimental)
- (2) Z. Tan, et. al, Rev. Sci. Instr. 60, (1989), 1021 (Math)
- (3) L. Troger, et. al., PRB 46, (1992), 3283 (mathematical)
- (4) Brewe, et. al., PRB 50, (1994) 9025 (Exp + Math)
- (5) Eisbitt, et. al. PRB 47, 1993, 14103 (Exp + Math)
- (6) Pfalzer, et. al. ,PRB 60, 1999, 9335 (Math)
- (7) C.H. Booth and F. Bridges, Archiv. Cond. Mat/ 0306252 V 1, 2003 (A program that does a math correction and does not neglect the fine structure contribution to the correction. Available from C. Booth.)

The last reference refers in part to an improved, public domain program for making these corrections, written by Corwin Booth. A useful web site for information is the Corwin Booth home page.

Pfalzer, et. al. point out that with small INCIDENT X-ray angle and normal EMERGENT X-ray angle the fluorescence distortion is EXASPERBATED. There can be a circumstance in which one would like to make the fluorescence distortion greater, not less. This type of application will be discussed later.

Diffraction Peaks in the Data

Consider the x-ray diffraction Ewald sphere interacting with the reciprocal lattice of a crystallite. Since the sphere radius is $(1/\lambda)$, in the course of an XAFS data scan, for which the incident photon energy is increased, the Ewald sphere constantly expands. When the sphere contacts a reciprocal lattice vector, especially in a fluorescence experiment, a diffracted beam can suddenly enter the fluorescence detector producing an unwanted artifact. There are numerous methods that can be applied separately or combined to alleviate this problem:

- (1) The standard filter – slit fluorescence detector system developed by Stern and Heald (Nuc. Instr. And Methods 172 (1980) 397) uses a filter that absorbs incident radiation more than fluorescence and therefore diminishes diffraction peaks in the data.
- (2) One can spin the sample with any simple motor, affixing a sample to the spinner with double stick tape. This “smears out” the reciprocal lattice intersection with the Ewald sphere and often works quite well in removing diffraction peaks.

- (3) Multi element energy dispersive detectors are quite good for this purpose. Not only can one use the energy discrimination to diminish detected diffraction, but the occasional strong peak that gets through the monochromator may show up on only one channel so that – if fortune smiles – there will be a few channels with no such peak in the entire scan.
- (4) I have seen people – in frustration over the diffraction peak problem, resort to grinding up a nice, flat polycrystalline ingot and perhaps mix the resulting powder with a binder. Fluorescence on such a specimen usually shows no diffraction peaks.
- (5) The glancing emergence angle method for minimizing fluorescence distortion tends to remove diffraction peaks also.

Combinations of methods can be used, of course, such as sample spinning plus a filter.

If the diffraction peaks are too strong relative to the fluorescence from the sample, they may significantly influence the data by *removing photons from the absorption process into the diffraction process*. I have heard of this effect, but have no personal experience suggesting methods to deal with such a problem.

Competing Edges

Often one must deal with absorption edges that interfere with the edge from the atomic species of interest. Filtering methods may fail because there are no filters that remove the unwanted edge without removing the desired signal. Multi – element energy dispersive detectors used for fluorescence detection may work if the background from the unwanted is not too intense. However, a problem that often presents itself is that energy dispersive detectors tend to saturate due to the signal they reject, which in itself distorts the data. The distortion effects can be subtle. A personal experience: In detection of Fe XAFS from dilute Fe in an alloy operation within the recommended parameters of the energy dispersive detector resulted in otherwise excellent looking data that exhibited something that looked like concentration dependent structural disorder!? As the Fe percentage increased, say from 1 to 2 %, the chi function wiggles in normalized spectra became more damped. By over de-tuning of the incident beam, the intensity of the fluorescence was reduced to well below the recommended limit for the detector. The “concentration dependent disorder” effect then disappeared.

(A stop gap method for a Z-1 concentrated matrix and a dilute Z element might be to maximize the fluorescence distortion of the concentrated Z-1 element to damp out those XAFS peaks as much as possible. Use glancing angle in and normal ray out.)

One solution to the problem of competing XAFS peaks is to use a monochromator for the fluorescence. A device based on log spiral bent silicon in the Laue mode has proven quite effective for such problems. (C. Karanfil. R. Sci. Instr. 73, no. 3, 2002, 1616). These devices are commercially available. Another approach has been to utilize flexible highly oriented pyrolytic graphite (HOPG) to produce a log spiral of revolution (LSR) device. (D. Pease, et. al. R. Sci. Instr. 71, 2000, 3267).

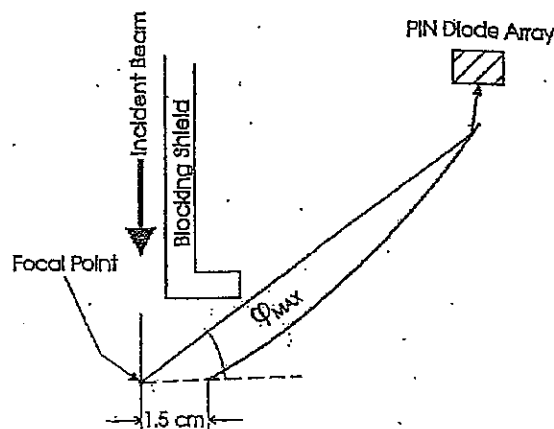
Both devices need to be optimized for particular wavelength regimes. The bent silicon log spiral has much better resolution. The LSR has better solid angle, on the order of 50% of the available 2π for first row transition elements. The bent silicon device is especially much better for higher energy ($> 10,000\text{eV}$) edges. *Both* devices require a focused beam.

Grant has discussed the bent laue monochromator. I will discuss new results and possibilities using the LSR device.

The curve of a log spiral was derived in the early 1600s by Descartes and is of the form in polar coordinates:

$$(1) \quad \rho = C \exp (\varphi / \tan \theta)$$

where C is a scaling factor, φ the polar angle, and θ the Bragg angle. The curve has the property that every ray that leaves a focus strikes the log spiral at angle θ . The LSR is made possible by a secret process developed in Russia by which *flexible* HOPG can be deposited layer by layer on a smooth surface such as smooth Plexiglas or diamond machined aluminum. The geometry is shown schematically below. The blocking shield prevents non monochromatized radiation from reaching the detector. The performance has now been markedly improved by the development of an annular ion chamber by Ed Stern, used instead of a PIN diode array.

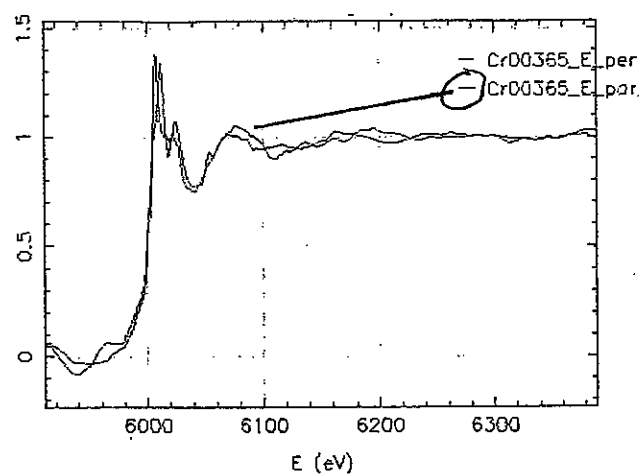
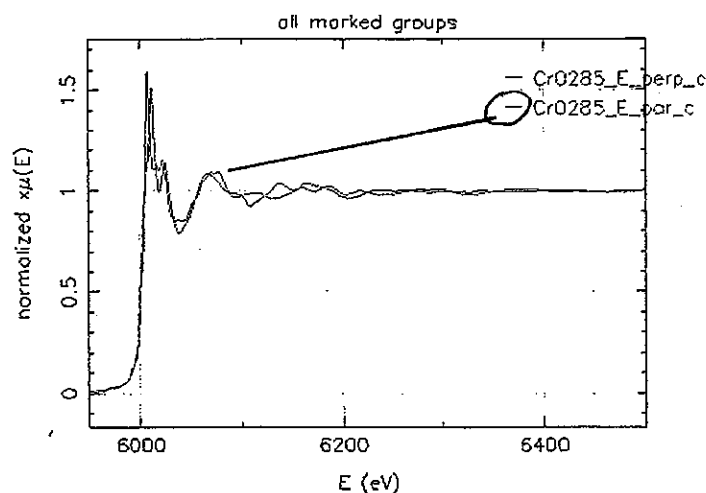


The device has been used – so far – for the following class of problems: Dilute edge of interest (Z) in a concentrated matrix (Z – 1) element. The Z-1 XAFS and noise can overwhelm the desired signal.

The limitation so far has been that the resolution of a LSR is ~ 200 eV in the range for first row transition elements, completely inadequate to detect the $K\alpha$ of the desired Z element and still reject the $K\beta$ of the matrix Z – 1 element. For Cr in V these lines are separated by only ~ 12 eV. Since the $K\beta$ lines are $\sim \times 10$ weaker than $K\alpha$ lines, the rejection of the Z-1 is limited to a factor of ten.

We point out two new developments:

- (1) Our present LSR has made it possible for us to obtain excellent data for the Cr edge in $(V_2O_3)_{1-x}(Cr_2O_3)_x$ with x down to .00365. For x at .00365 there are some residual V oscillations. We believe we can correct for these using a filtering technique.
- (2) We now believe we have a way to remove the problem of the Z-1 $K\beta$ line in the LSR data by a new method of operation.



The above data were obtained at the PNC – CAT line at the APS

Left: insulating phase

$x = .0285$

Single xtal: $E \perp C$

$E \parallel C$

Right: conducting phase

$x = .00365$

Single xtal $E \perp C$

$E \parallel C$

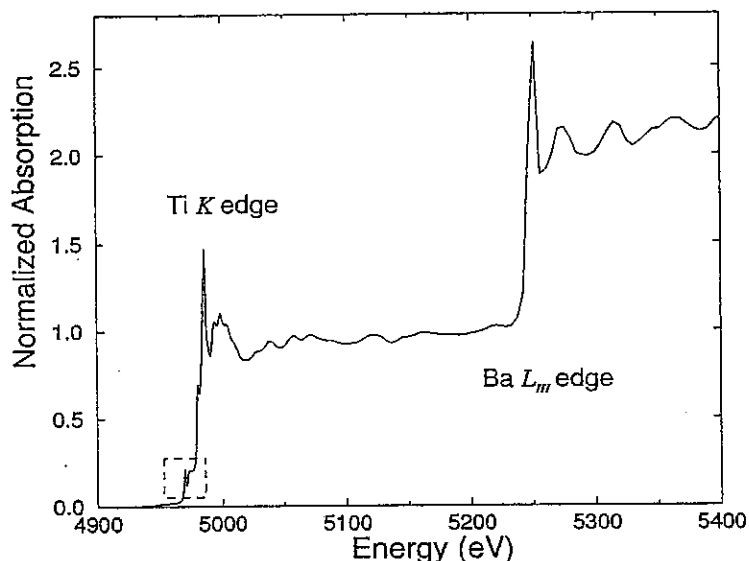
[See residual V XAFS]

We believe we can correct for the residual V XAFS oscillations in the $x = .00365$ sample with a filtering technique I will describe.

Mahalingham Balasubramanian has pointed out to us that using the LSR and the insertion device at the PNC – CAT line we have sufficient intensity to do these experiments with a LSR optimized for the Cr K_{β} line. Then all V lines will be repressed! In fact the signal to noise will be about the same, but with repression of the V XAFS at the Cr edge. Using the K_{α} line of Cr the background for a 1% Cr sample in 99% V, coming from the V K_{β} line is ~ 10 times the desired signal assuming complete removal of the V K_{α} line. (We observe that indeed, the LSR designed for Cr K_{α} decreases the V background from $x 100$ to $x 10$ the Cr edge jump). With a LSR optimized for Cr K_{β} instead of Cr K_{α} the Cr intensity is reduced by a factor of ten and the V background is removed. Under these circumstances the signal to noise ratio is about the same for both cases, but now the V oscillations are completely removed from the Cr edge. Bonus! A LSR for Cr K_{β} is also good as a LSR for Mn K_{α} in case we wish to use the device on Mn edges.

The “Negative Absorption Effect” Artifact

There is a “worse case scenario” in which an interfering edge is intense and in the middle of the XAFS range of the desired edge. A well known example in the Ba L_3 edge that interferes with the Ti K edge in BaTiO₃. The data below is taken from the thesis of Bruce Ravel.



Even if a monochromator has sufficient resolution to remove the unwanted emission line from the fluorescence, the data is ruined because the unwanted emission line *removes photons from the desired absorption channel*. Shown below is a Cr K edge in a Cr₈₀Mn₂₀ alloy with an HOPG monochromator tuned to remove the Mn K _{α} line. The circled region shows a “negative Mn absorption edge” because of this effect. There may be no way around this problem? (Any suggestions welcome.)

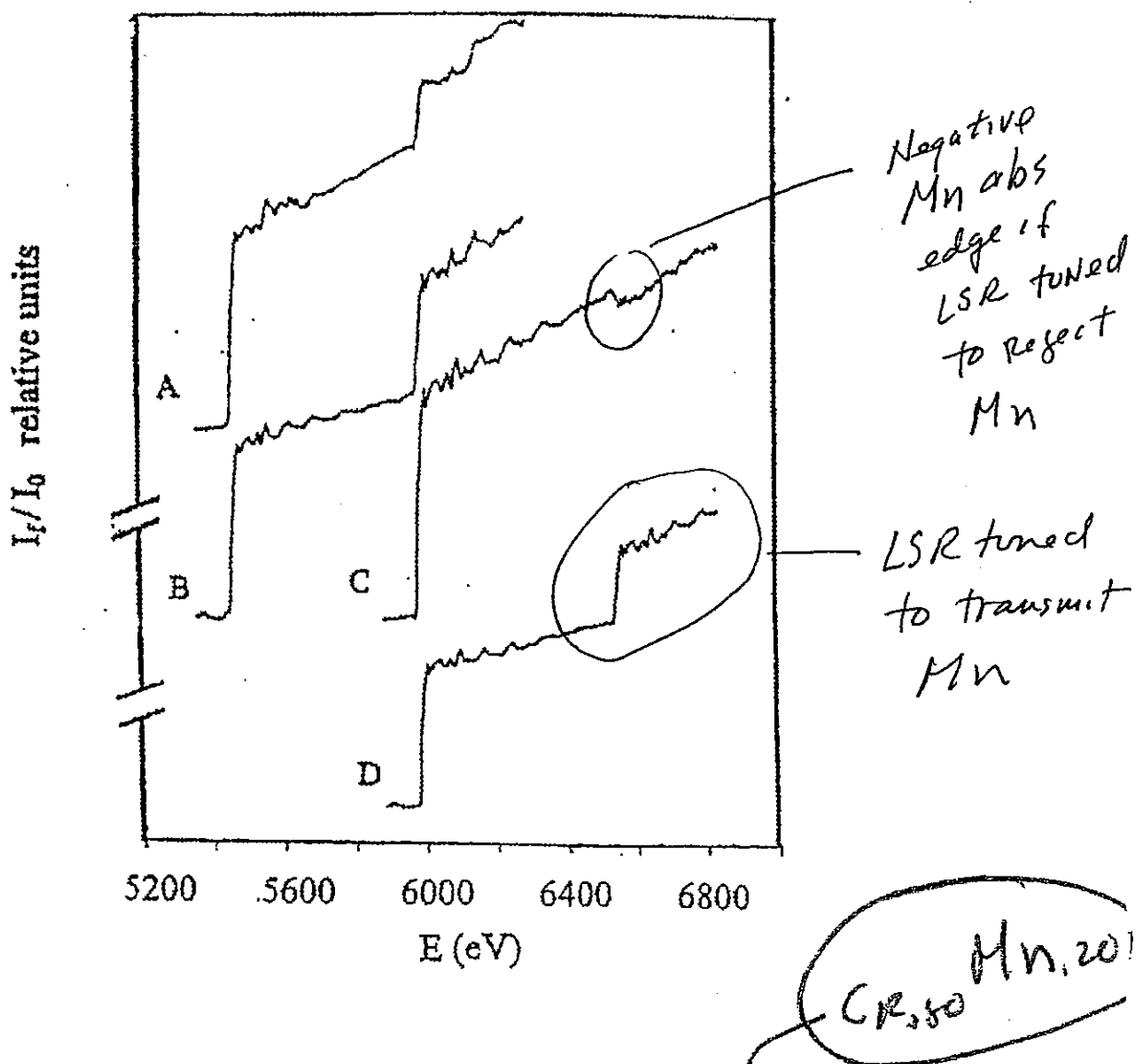


Fig. 2 A, LSR set to transmit both V and Cr edges of a $V_{.80}Cr_{.15}Ti_{.05}$ alloy, blocking shield removed to allow transmission of diffraction peaks; B, same as A but with blocking shield in place to remove diffraction peaks; C, $Cr_{.80}Mn_{.20}$ alloy XAFS, LSR tuned to transmit Cr but reject Mn K_{α} ; D, same as C but with LSR tuned to transmit both Cr and Mn K_{α} (Pease, 2000).

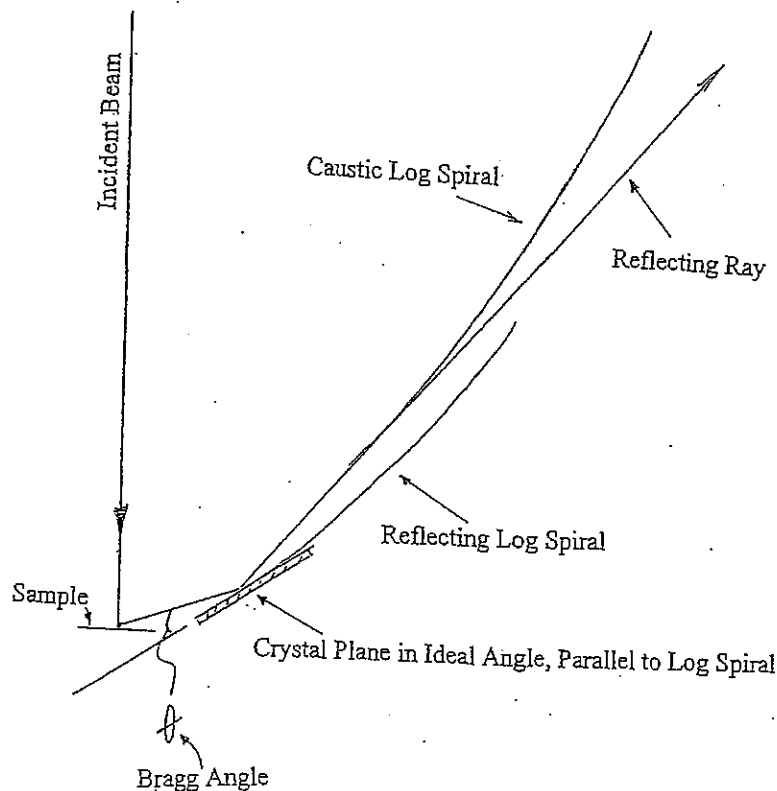
Another Interesting Property of the Log Spiral Shape

Descartes: about 1620: $\rho = C_1 \exp(\phi / \tan \theta)$

Jacob Bernoulli: about 1693: For every log spiral there is a "caustic" which is another log spiral. That is, the rays reflecting from a log spiral are all tangent to a second log spiral. I *believe* that the caustic has the same equation as above but with a scaling factor C_2 such that:

$$C_2 / C_1 = 2 \cos(\theta) / \exp(\theta / \tan \theta)$$

This is interesting. For a more common monochromator shape such as the Johannson ground and bent crystal, the beam is focused and one can improve resolution at some cost in intensity by narrowing a slit. But a log spiral does not produce a focused beam. In stead it has a caustic. Below is a sketch of a log spiral for Cu K_α and its caustic.



Consider a crystal plane such that the plane is not parallel to the log spiral surface but at an angle such that the ray incident from the log spiral focus strikes the crystal at an angle greater than the ideal Bragg angle. The corresponding diffracted ray corresponds to an energy less than the desired energy. But such rays will be blocked by the caustic, and therefore removed from the low energy portion of the HOPG transmission window.

In principle, one can then do the following. Combine a log spiral of revolution with a caustic of revolution made of aluminum, say. For HOPG angles from the mosaic spread that are greater than ideal (passing too low energies) the caustic will block such beams. For HOPG, since the mosaic spread is ~ 1 eV, it is conceivable that one could do this, although the alignment and machining would be most challenging. Say the ideal energy is E_0 . One would then approach a high pass filter which would allow energies to pass from E_0 to $\sim E_0 + 100$ eV, and block energies less than E_0 if the alignment and machining were good enough.

Such a LSR is a high pass filter.

An absorption foil is a low pass filter

These could be combined. One could envision applications in inelastic scattering XAFS. But it would be hard to do this.